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(54) POLYLACTIC ACID STEREOCOMPLEX POLYMER COMPOSITION

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain a highly crystalline polylactic acid stereocomplex polymer composition having excellent moldability and processability at a low cost and various kinds of molded and processed products comprising the polymer.
SOLUTION: This crystalline polylactic acid stereocomplex polymer composition is obtained by blending an amorphous polymer (A) constituted of 70-95 mol.% of an L-lactic acid unit and 5-30 mol.% of a D-lactic acid unit and/or a copolymerizable component unit except lactic acid with an amorphous polymer (B) constituted of 70-95 mol.% of the D-lactic acid unit and 5-30 mol.% of the L-lactic acid unit and/or the copolymerizable component unit except the lactic acid in the blending ratio of the component A:B of 10:90 to 90:10 by weight in a molten state.

CLAIMS

[Claim(s)]
[Claim 1]Amorphous polymer (A) constituted by 70-95 mol of L-lactic acid unit %, and D-lactic acid unit and/or 5-30 mol of copolymerization component unit % other than lactic acid, Amorphous polymer (B) constituted by 70-95 mol of D-lactic acid unit %, and L-lactic acid unit and/or 5-30 mol of copolymerization component unit % other than lactic acid, (A): (B) A crystalline polylactic acid stereo complex polymer composition obtained by carrying out a melting blend by a mixed weight ratio of the range of =10:90 - 90:10.
[Claim 2]The stereo complex polymer composition according to claim 1 whose weight average molecular weight of said amorphous polymer (B) weight average molecular weight of said amorphous polymer (A) is 1000-400,000, and is 1000-400,000.
[Claim 3]An injection molding article which becomes claim 1 or the 2nd paragraph from a stereo complex polymer composition of a statement, An extrusion cast, a vacuum pressure sky cast, a blow molding article, a film, a sheet, a nonwoven fabric, textiles and cloth, a complex with other materials, materials for agriculture, materials for horticulture, materials for fishings, engineering works and structural materials, stationery, medical supplies, or other casts.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to a polylactic acid stereo complex polymer composition. This invention relates also to the various fabricating-operation articles which become since it consists of said stereo complex polymer composition.
[0002]Polylactic acid stereo complex polymer is a mixture of Polly L-lactic acid (PLLA) and Polly D-lactic acid (PDLA). By making polylactic acid into stereo complex polymer, the following feature is revealed, for example.
(1) From an independent thing, a PLLA chain and a PDLA chain have strong cohesive force respectively, and show high crystallinity.
(2) The melting point becomes high and its thermal stability improves. Tg does not change.
(3) Draw magnification improves in the case of manufactures of textiles, films, etc., and

the thing of a high property value is obtained. Although a fabricating operation can be carried out at the same temperature as PLLA, the melting point of what carried out the stretch orientation becomes high.

[0003]

[Description of the Prior Art]As a manufacturing method of polylactic acid, the lactide which is a cyclic dimer of lactic acid to lactic acid is compounded, and the method of obtaining polymer by this ring opening polymerization and the method by the direct polymerization from lactic acid are known.

[0004]How (JP,7-118259,A) to obtain lactide from lactic acid by reaction evaporation as a lactide method, for example, The method (US JP,5,142,023,B specification, the No. 5,359,026 specification) of rectifying the straight chain dimer mixed in the case of reaction evaporation, a trimer, etc. after toluene, the method (JP,7-138253,A) of carrying out crystallization with ethyl acetate, and reaction evaporation, etc. are indicated. The method of carrying out azeotropy of a solvent and lactide, such as xylene, is also indicated (US JP,5,420,304,B specification).

[0005]The direct polymerization method (BP 779,291) in the inside of xylene or toluene is indicated, and the method (JP,6-65360,A) using the solvent of high boiling points, such as diphenyl ether, is indicated.

[0006]Although 3000-5000 were conventionally made into the limit depending on massive direct polymerization as for the polymerization average molecular weight, according to the special playback common No. 828482 [seven to] gazette, with a weight average molecular weight of 50,000 or more polymer is obtained by using the catalyst of a silicic acid aluminum system. The above conventional technology is PLLA, PDLA, or PDLLA (what polymerized from the raw material which contains D and L lactic acid at an arbitrary rate.). Usually, random polymer. It is related with a process.

[0007]On the other hand, high crystallinity is required of the polylactic acid used for textiles or an oriented film, and not less than 99% of PDLA has [L object content] desirable PLLA or D object content of not less than 99%. Also in the sheet or the injection-molding thing, not less than 95% of PDLA is desired [L object content] for PLLA or D object content of not less than 95%.

[0008]However, even if it uses lactic acid of 99% of L purity for a raw material noting that I will obtain PLLA of high L object content, racemization of lactic acid happens for an elevated temperature and a prolonged reaction, and L purity falls. Then, in the lactide method, by removing meso lactide by crystallization, rectification, etc. conventionally, the purity of LL-lactide is raised and polymer of not less than 99% of L object content is manufactured. Although lactic acid of 50 to 70% of L purity or lactide obtained from refining residue at this time returns that part to a raw material and is lowering and using L object content by permissible within the limits, since crystallinity falls, that use is restricted.

[0009]On the other hand, as for a film, textiles, the injection molding thing, the nonwoven fabric, and the sheet, piezo-electricity and a pyroelectric element are expected crystallinity still higher than the crystallinity which the polylactic acid of a 100%L object or a 100%D object has from the first.

[0010]The lactic acid currently incidentally manufactured industrially is L-lactic acid (98 to 99% of L purity, bacterial coupling), or racemic lactic acid (D and L are 1:1 and a chemosynthesis method). In industrialization of this invention, although D-lactic acid is

required, D-lactic acid is easily producible by changing the microorganism kind at the time of lactic acid fermentation. That is, D-lactic acid is producible if Lactobacillus delbrueckii, Bacillus laevolactis, etc. are used.
[0011]Polly L-lactide and Polly D-lactide are dissolved in organic solvents, such as chloroform, respectively, and the resin composition blended according to solution states by the weight ratios 10:90-90:10 is indicated by JP,5-48258,B. And the absorbable surgical suture used as a use at the material of division absorptivity, for example, in the living body, The film for separation of industrial use, etc. are indicated further the cultivation film for agriculture and textiles, such as a bone plate, an artificial tendon, a synthetic ligament, an artificial blood vessel, and a medicinal sustained-release carrier, the rope, the sustained-release carrier of agricultural chemicals, etc.
[0012]Since Polly L-lactide and Polly D-lactide become uniform, this method of using a solvent can form stereo complex polymer good. Therefore, it is thought that it is suitable for production of a small amount of materials by high-value added, such as medical use. However, since it is necessary to volatilize a solvent, to manufacture of industrial general-purpose material, it is unsuitable in respect of cost.
[0013]The matrix for drug delivery which becomes the Patent Publication Heisei No. 501109 [four to] gazette from poly (S-lactide) and poly (R-lactide), and thread are indicated. In this gazette, chloroform, methylene chloride, chlorinated methane, Each polymer is dissolved in solvents, such as sulfolane, N **MECHIRU pyrrolidone, dimethylformamide, a tetrahydrofuran, a butyrolactone, a trioxane, and hexafluoro isopropanol, and the method of evaporating an after-mixing solvent is indicated. The mold releasing film of the discharge carrier with the passage of time for the absorptivity sewing thread used in the living body, the table, an artificial tendon, a synthetic ligament, an artificial blood vessel, and medication, the film for cultivation in agriculture, the textile rope, the carrier for discharge with the passage of time of agricultural chemicals, and the industrial use way is indicated as a use. Mixing by a molten state and extension of textiles are also described. However, to manufacture of general-purpose material, it is unsuitable in respect of cost.
[0014]Polylactic acid complex textiles are indicated by JP,63-264913,A.
It is shown by by extending the textiles which carried out spinning of the mixed material in the solution states of Polly L-lactide and Polly D-lactide that the intensity of textiles increases.
It is indicated that the optical purity of the Polly L-lactide used here and Polly D-lactide is not less than 90%. As a use, for a non-drawn fiber or the textiles of low draw magnification. Since it has porous structure, if it uses as a hollow fiber, the application as medical fibers, such as the absorbable surgical suture used in the living body, an artificial tendon, a synthetic ligament, an artificial blood vessel, a bone plate, and a reinforcing member of a screw, and also the rope and textiles of general industrial use is shown. [the textiles for separation of a gas or a fluid, and]
[0015]It becomes JP,63-241024,A from poly (R **RAKUCHIDO) a portion and a poly (S-lactide) portion, The polymer composition, wherein at least one above-mentioned portion is a polymer composition which is a part of copolymerization and this constituent fuses at an elevated temperature rather than one of portions in that case is indicated.
[0016]
[Problem(s) to be Solved by the Invention]The purpose of this invention is to provide the

polylactic acid stereo complex polymer composition of high crystallinity excellent in molding workability. The purpose of this invention is also to provide the various fabricating-operation articles which consist of said polylactic acid stereo complex polymer.
[0017]
[Means for Solving the Problem]As a result of inquiring wholeheartedly, by carrying out the melting blend of the amorphous polymer of a specific presentation which uses as the main ingredients amorphous polymer and D-lactic acid of a specific presentation which uses L-lactic acid as the main ingredients by a specific mixed weight ratio, this invention persons found out that the above-mentioned purpose was attained, and completed this invention.
[0018]Namely, amorphous polymer (A) from which this invention was constituted by 70-95 mol of L-lactic acid unit %, and D-lactic acid unit and/or 5-30 mol of copolymerization component unit % other than lactic acid, Amorphous polymer (B) constituted by 70-95 mol of D-lactic acid unit %, and L-lactic acid unit and/or 5-30 mol of copolymerization component unit % other than lactic acid, (A): (B) It is the crystalline polylactic acid stereo complex polymer composition obtained by carrying out a melting blend by a mixed weight ratio of the range of =10:90 - 90:10.
[0019]In this invention, weight average molecular weight of said amorphous polymer (A) is 1000-400,000, and it is preferred that weight average molecular weight of said amorphous polymer (B) is 1000-400,000.
[0020]An injection molding article in which this invention consists of said stereo complex polymer composition, They are an extrusion cast, a vacuum pressure sky cast, a blow molding article, a film, a sheet, a nonwoven fabric, textiles and cloth, a complex with other materials, materials for agriculture, materials for horticulture, materials for fishings, engineering works and structural materials, stationery, medical supplies, or other casts.
[0021]In this invention, it uses with "polylactic acid" in a meaning also containing polylactide (polylactic acid obtained by ring opening polymerization of lactide).
[0022]
[Embodiment of the Invention]In this invention, amorphous polymer (A), i.e., Polly L-lactic acid, is the polylactic acid constituted by the L-lactic acid unit 70 - 95-mol %, and D-lactic acid unit and/or copolymerization component units 5 other than lactic acid - 30-mol %.
[0023]If the L-lactic acid unit in Polly L-lactic acid will be less than [70 mol %] and D-lactic acid unit exceeds 30-mol %, crystalline polylactic acid stereo complex polymer will become is hard to be obtained. On the other hand, when an L-lactic acid unit exceeds 95-mol %, Polly L-lactic acid changes easily with a crystalline thing.
[0024]Amorphous polymer (B), i.e., Polly D-lactic acid, is the polylactic acid constituted by **, the D-lactic acid unit 70 - 95-mol %, and an L-lactic acid unit and/or copolymerization component units 5 other than lactic acid - 30-mol %.
[0025]If D-lactic acid unit in Polly D-lactic acid will be less than [70 mol %] and an L-lactic acid unit exceeds 30-mol %, crystalline polylactic acid stereo complex polymer will become is hard to be obtained. On the other hand, when D-lactic acid unit exceeds 95-mol %, Polly L-lactic acid changes easily with a crystalline thing.
[0026]As copolymerization monomer components other than lactic acid in amorphous

polymer (A) and/or amorphous polymer (B), They are a lactic acid monomer or lactide, and other copolymerizable monomer components, Dicarboxylic acid, polyhydric alcohol, hydroxycarboxylic acid, lactone, etc. with the functional group of two or more ester bond plasticities; And various polyester, various polyether, various polycarbonate, etc. which comprise the constituent of these versatility are mentioned.
[0027]As dicarboxylic acid, succinic acid, adipic acid, azelaic acid, sebacic acid, terephthalic acid, isophthalic acid, etc. are mentioned.
[0028]Aromatic polyhydric alcohol, such as what carried out the addition reaction of the ethylene oxide to the bisphenol as polyhydric alcohol, Ethylene glycol, propylene glycol, butanediol, hexandiol, Octanediol, glycerin, sorbitan, trimethylolpropane, Ether glycols, such as aliphatic polyhydric alcohol, such as neopentyl glycol, a diethylene glycol, triethylene glycol, a polyethylene glycol, and a polypropylene glycol, etc. are mentioned.
[0029]As hydroxycarboxylic acid, what is indicated to glycolic acid, hydroxybutylcarboxylic acid, and other JP,6-184417,A is mentioned.
[0030]As lactone, glycolide, epsilon-caprolactone glycolide, epsilon-caprolactone, beta propiolactone, delta-butyrolactone, beta- or gamma-butyrolactone, PIBARO lactone, delta-valerolactone, etc. are mentioned.
[0031]As a manufacturing method of polylactic acid (polymer (A), (B)), known arbitrary polymerization methods are employable. Being known most typically may carry out the condensation polymerization of the lactic acid directly, although it is the method (the lactide method) of carrying out ring opening polymerization of the lactide which is an anhydrous cyclic dimer of lactic acid. Organotin compounds, such as octylic acid tin, are usually used for a polymerization reaction.
[0032]In this invention, the ranges of the weight average molecular weight of amorphous polymer (A) are 1000-400,000, and, as for the weight average molecular weight of amorphous polymer (B), it is preferred that it is the range of 1000-400,000. The weight average molecular weight of amorphous polymer (A) and amorphous polymer (B) has the more preferred range of 50,000-400,000.
[0033]however, the stereo complex polymer composition of high crystallinity of this invention -- 1000 to about 10,000 -- it is comparatively obtained also from Polly L-lactic acid of the amorphism nature of low molecular weight, and Polly D-lactic acid, and gets. Here, it is the advantage of this invention. That is, the quality of the lactide of a raw material is bad (it is an implication about moisture or a straight chain low molecule), and even if the molecular weight of Polly L-lactic acid and/or Polly D-lactic acid does not become high enough, it is possible to consider it as a stereo complex polymer composition usable as general-purpose resin. About 1000 molecular weight number [which could simplify the lactide purification process by this, or was directly obtained by dehydration condensation] polymer can also be used.
[0034]In this invention, the melting blend of amorphous polymer (A) and the amorphous polymer (B) is carried out by the mixed weight ratio of the range of (A):(B) =10:90 - 90:10. Crystalline polylactic acid stereo complex polymer becomes is it hard to be obtained that a mixed weight ratio is outside this range. The ranges of the desirable mixed weight ratio of polymer (A) and polymer (B) are (A):(B) =30:70 - 70:30, for example. However, this desirable range is a value which changes with the presentations of amorphous polymer (A) and amorphous polymer (B) itself, and in order to acquire crystallinity suitable for the target molding, it is good [the range] to set suitably.

[0035]Although the cooking temperature in particular at the time of carrying out the melting blend of amorphous polymer (A) and the amorphous polymer (B) is not limited, it is usually about 170-220 **.
[0036]Using said polylactic acid stereo complex polymer composition, an injection molding article, An extrusion cast, a vacuum pressure sky cast, a blow molding article, a film, a sheet, a nonwoven fabric, textiles and cloth, a complex with other materials, the materials for agriculture, the materials for horticulture, the materials for fishings, engineering works and structural materials, stationery, medical supplies, or other casts can be obtained. Shaping can be performed with a conventional method.
[0037]To the constituent in this invention, if needed A conventionally publicly known plasticizer, Various additive agents, such as an antioxidant, a thermostabilizer, light stabilizer, an ultraviolet ray absorbent, paints, colorant, various fillers, a spray for preventing static electricity, a release agent, perfume, lubricant, fire retardant, a foaming agent, a bulking agent, antibacterial properties and an antifungal agent, and a nucleation agent, may be blended. Or when manufacturing stereo complex polymer, these additive agents may be blended.
[0038]
[Example]Although an example is given to below and this invention is explained to it still more concretely, this invention is not limited to an example.
[Example 1] to what added D-lactide by Purac to 95 % of the weight of Shimadzu L-lactide 5% of the weight. Octylic acid tin was taken out as a strand about 3 mm in diameter after the polymerization reaction for 200 ** and 30 minutes with the biaxial kneading machine made from 200 weight ppm **** and KURIMOTO (S-1), and it cut after cooling in the tank, and cut into about 6 mm in length with the strand cutter, and the PLLA pellet was created. Except on the other hand having used as lactide what added Shimadzu L-lactide to 95 % of the weight of D-lactide by Purac 5% of the weight, same operation was performed and the PDLA pellet was created.
[0039]Thus, each PLLA(s) and PDLA(s) which were created were a transparent amorphous state. When weight average molecular weight was measured in GPC, PLLA was 185,000 and PDLA was 180,000. When DSC measurement was performed, it became clear that a glass transition point (Tg) was observed by 58 **, and any pellet was amorphous polymer.
[0040]After blending 210 ** of equivalent weight (weight) of a PLLA pellet and a PDLA pellet for 10 minutes with the biaxial kneading machine made from KURIMOTO (S-1), it took out as a strand about 3 mm in diameter, and it cut after cooling in the tank and it was cut into about 6 mm in length with the strand cutter. Thus, the created blend polymer was a transparent amorphous state. It was 175,000 when weight average molecular weight was measured in GPC. When DSC measurement was performed, the crystallizing point (Tc) was observed by 122 **, the melting point (Tm) was observed by 194 **, and it has checked that it was a crystalline polymer.
[0041][Examples 2-4 and comparative examples 1-2] About Examples 2-4 and the comparative examples 1-2, except having changed the compounding ratio of the object for PLLA composition and L object of the lactide for PDLA composition, and D object into the value shown in Table 1, the same polymerization conditions and operation as Example 1 were performed, and each PLLA pellet and each PDLA pellet were obtained. As a result of DSC measurement, the glass transition point (Tg) was observed and each of

these PLLA(s) pellets and PDLA pellets was amorphous polymer.
[0042]Next, except having changed the compounding ratio of the polymer PLLA and PDLA into the value shown in Table 1, the same blend operation as Example 1 was performed, and each blend polymer was created. DSC measurement was performed about each blend polymer. A result is shown in Table 1.
[0043]About Examples 2-4, a crystallizing point (Tc) and the melting point (Tm) were observed, and it checked that it was a crystalline polymer. About the comparative examples 1-2, a crystallizing point (Tc) and the melting point (Tm) were not observed, but it was amorphous polymer.
[0044]
[Table 1]

	原料ラクチド		ポリマーPLLA及びPDLA						ブレンドポリマー				
	配合比（重量比）		分子量（×10⁴）		DSC PLLA		DSC PDLA		配合比（重量比）	分子量（×10⁴）	DSC		結晶状態
	PLLA用 L:D	PDLA用 L:D	PLLA	PDLA	Tg（℃）	Tm（℃）	Tg（℃）	Tm（℃）	PLLA:PDLA		To（℃）	Tm（℃）	
実施例1	95:5	5:95	18.5	18.0	58	なし	58	なし	50:50	17.5	122	194	結晶性
実施例2	70:30	10:90	17.5	17.5	55	なし	57	なし	10:90	17.0	125	186	結晶性
実施例3	80:20	5:95	18.0	18.0	56	なし	58	なし	90:10	17.5	128	180	結晶性
実施例4	70:30	5:95	17.0	18.5	55	なし	58	なし	30:70	18.0	126	182	結晶性
比較例1	65:35	10:90	17.5	17.5	52	なし	57	なし	50:50	17.0	なし	なし	非晶性
比較例2	90:10	10:90	18.0	17.5	57	なし	57	なし	5:95	17.5	なし	なし	非晶性

[0045]
[Effect of the Invention]According to this invention, the polylactic acid stereo complex polymer composition of high crystallinity excellent in molding workability is provided by low cost. According to this invention, the various fabricating-operation articles which consist of said polylactic acid stereo complex polymer composition are provided.

[Translation done.]